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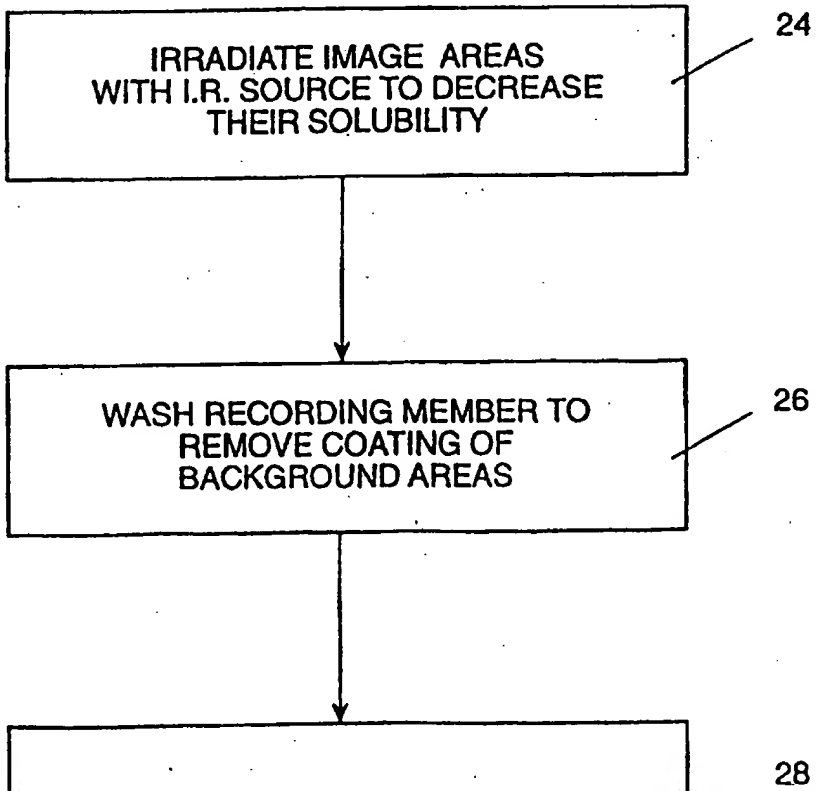
Published
With international search report.

(54) Title: A RECORDING FILM FOR PRODUCING A PRINTING PLATE THEREFROM

(57) Abstract

An image recording member and a method for producing a recording film therefrom is provided. The image recording member includes a substrate layer and an infrared (IR) sensitive coating, the solubility of which being affected by impingement of IR radiation thereon. In accordance with one embodiment of the invention, the substrate layer is formed substantially of polyester or polycarbonate with a thickness generally between 50 and 350 microns and the transmissivity of the substrates to ultraviolet radiation is substantially higher than that of the coating.



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A RECORDING FILM FOR PRODUCING A PRINTING PLATE THEREFROM

FIELD OF THE INVENTION

The present invention relates to Infra-Red sensitive recording members, to methods for producing same and to methods for producing a recording film therefrom.

BACKGROUND OF THE INVENTION

Recording members and methods for producing recording films therefrom, for example for the graphic arts and printing industries, are well known in the art. Similarly, the use of Infra-Red (IR) radiation, usually employing a laser beam to image them so as to produce a recording film with a representation of an image thereon is known in the art.

Generally speaking prior art recording members fall into two categories, namely, silver based recording members and ablation or ablation transfer based recording members.

SUMMARY OF THE INVENTION

The present invention provides improved recording members, methods for producing same and methods for producing a recording film therefrom.

There is thus provided, in accordance with the present invention, an image recording member which includes a substrate layer and an infra red (IR) sensitive coating, the solubility of which being affected by impingement of IR radiation thereon.

In accordance with a preferred embodiment, the substrate layer is formed substantially of polyester or polycarbonate with a thickness generally

between 50 and 150 microns. Further, the transmissivity of the substrate to Ultra-Violet radiation is substantially higher than that of said coating.

In accordance with yet another preferred embodiment the solubility of the coating increases upon impingement of said IR energy thereon, the pattern representing said image being a positive of said image. In the preferred embodiment, the coating includes a resin and an Infra-Red absorbing material and may also include a cross-linking agent. The resin is preferably selected from the group consisting of polyurethane, polyacrylate, polyester, vinylacrylate, phenolic resins and esterified resins, the IR absorbing material is selected from the group consisting of carbon black, nigrosine, phthalocyanine dye, metal diethylene and triaryl methane cationic salts, and the cross linking agent is selected from the group consisting of benzoyl peroxide, aziridine cross-linker, ammonia and phenol formaldehyde cross-linking resin.

In an alternative embodiment, the solubility of the coating decreases upon impingement of the IR energy thereon, the pattern representing the image being a negative of the image.

There is also provided, in accordance with a preferred embodiment of the present invention, a method for producing an image recording member which includes the steps of providing a substrate layer and coating the substrate layer with an infra red (IR) sensitive coating, the solubility of which being affected by impingement of IR radiation thereon. The method further includes the steps for producing the recording members of the present invention.

There is further provided, in accordance with a preferred embodiment of the present invention, a method for producing an image sensitive recording film which includes the steps of:

a. providing a recording member comprising an ultra violet transparent substrate layer and an infra red (IR) sensitive coating, the solubility of which being affected by impingement of IR radiation thereon;

b. Affecting the solubility of an area of the recording member; and

c. Washing the recording member so as to substantially remove the coating so as to expose the substrate layer, whereby a recording film with a representation of an image is formed.

In accordance with a preferred embodiment of the present invention, the step of affecting the solubility of an areas of the coating of the recording member includes the step of increasing the solubility of the areas by impinging IR energy thereon. Further, the step of impinging is upon the background areas around the areas representing the image. Alternatively, the impinging is upon the image areas.

In accordance with an alternative preferred embodiment of the present invention, the step of affecting the solubility of an areas of the coating of the recording member includes the step of decreasing the solubility of the areas representing the image by impinging IR energy thereon.

Finally, there is provided in accordance with the present invention a recording film produced by the method for producing same from the recording members of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be understood and appreciated more fully from the following detailed description taken in conjunction with the appended drawings in which:

Fig. 1 is a schematic illustration of recording member, constructed and operative in accordance with a preferred embodiment of the present invention;

Fig. 2 is a schematic block diagram illustration of a method for producing a recording film from the recording member of Fig. 1 according to a preferred embodiment of the present invention;

Fig. 3 is a schematic block diagram illustration of a method for producing a recording film from the recording member of Fig. 1 according to another preferred embodiment of the present invention; and

Fig. 4 is a schematic block diagram illustration of yet another method for producing a recording film from the recording member of Fig. 1 according to a further preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

Reference is now made to Fig. 1 which illustrates the recording member of the present invention. The recording member, generally referenced 10, comprises a substrate layer 12 formed of one or more layers of a material transparent to Ultra-Violet (UV) radiation, such as polyester. Recording member 10 also comprises one or more coatings, generally referenced as coating 14 coated on substrate layer 12. A particular feature of coating 14 is that its solubility changes upon impingement of IR radiation thereupon as described in detail hereinbelow.

Coating 14 comprises a resin, preferably a film forming resin, such as polyurethane, polyacrylate, polyester, vinylacrylate, phenolic and esterified resins. Coating 14 also comprises an IR absorbing material, such as carbon black and in some instances, a cross-linking agent as described in detail hereinbelow.

According to a first embodiment of the present the resin mixture of coating 14 cross-links upon impingement of IR radiation thereon, whereby the solubility of the image area exposed to the IR radiation decrease, i.e. cross linking within the resin mixture insolubilizes the areas of the recording member on which a representation of an image is to be recorded.

According to a first preferred embodiment of the present invention, coating 14 includes a cross linking material which insolubilizes the resin upon impingement of IR radiation thereon. For this type of coating, a preferred method of producing a recording film from the recording member 10 is illustrated in Fig. 2. The method includes the step 24 of employing a laser to irradiate the area of the coating representing the image with IR radiation absorbed by the IR absorbing material of coating 14. The IR radiation source is preferably an IR laser diode or

area or images areas if more than a single image is recorded on recording member 10.

The method further includes the step 26 of washing the recording member after the irradiation thereof. The washing clears the background areas of the recording member, i.e. the areas of the recording member which do not represent the image to be recorded and the solubility of which did not decrease due to the irradiation step, so as to remove the coating in the background areas and to expose substrate layer 12.

According to an alternative preferred embodiment of the present invention (Fig. 3), the background is irradiated as indicated in step 34 so as to increase the solubility thereof. The recording member is then washed as indicated by step 36 similarly to step 26 so as to receive recording film 38.

A preferred coating 14 for the method of the embodiment of Fig. 3 includes a relatively small amount of cross-linking agent or does not include a cross linking agent at all so as to avoid insolubilization of the imaged area. Rather, the irradiation step 34 causes absorption of IR energy by the IR absorbing material and weakening or breakage of bonds of the resin so as to facilitate washing of the background during step 36.

It will be appreciated that the present invention is not limiting to the steps of irradiating the background areas so as to increase their solubility. According to an alternative embodiment of the present invention illustrated in Fig. 4, the image areas are irradiated to increase the solubility thereof as indicated by step 44, the recording member is than washed as indicated by step 46 so as to clear the image areas and to form a negative recording film 48.

The following examples are non limiting examples of certain aspects of the present invention. All quantities quoted are in parts by weight.

EXAMPLE I

Example I is a non limiting example for a recording member suitable for imaging in accordance with the method of Fig. 2 where the IR radiation insolubilizes coating 14.

Fifty (50) parts of a Witcobond 234 (aliphatic anionic colloidal aqueous polyurethane dispersion manufactured by Witco of the U.S.A) resin was mixed with 150 parts of StanTone 90WD01 (carbon dispersion in water/acrylic - manufactured by Harwick of the U.S.A).

The mixture was coated with a wire rod onto 100 micron clear polyester film (substrate layer 12). The recording member was dried in an oven at 120°C for 30 seconds. The dry recording member weight was 0.7 grams per square centimeter. The resulting IR sensitive recording member was imaged on an external drum system using a half watt laser diode emitting at 870 nanometers. A somewhat faint image was visible on the surface of the black film. The film was then washed with benzyl alcohol which easily removed the background material, leaving a sharp black image corresponding to the areas where the laser beam irradiated the film. The heat produced during imaging insolubilized the resin mixture of polyurethene and acrylic resin.

EXAMPLE II

Example II is a non limiting example for a recording member suitable for imaging in accordance with the method of Fig. 3 where the IR radiation solubilized the background areas of coating 14.

50 parts of Neorez 9679 (Zeneca - water-borne aliphatic polyester urethane polymerwere) resin were mixed with 100 parts of StanTone 90WD01 (see example I), 5 parts water, 3.5 parts Neocryl CX-100 (room temperature

cross-linking agent) and 2.5 parts Ektasolve EP (Kodak - 2-propoxy ethanol coalescing solvent).

The mixture was bar coated onto clear 100 micron polyester film and was dried in an oven at 120°C for 3 minutes to a coating weight of 1.2 grams per square meter. Imaging was as described in Example I. In this case, the IR radiation caused bond weakening and/or bond destruction, resulting in an increase in solubility of the imaged areas. The imaged film was washed with a 50% mixture of water and ethyl lactate and the irradiated background areas were washed to provide a clear transparent substrate layer. Dmax, i.e. the maximal transmissivity to UV radiation was 4.0 and Dmin, i.e. the minimal transmission density of the washed areas was 0.06. It will be appreciated that smaller transmission density indicates higher transmissivity to UV radiation.

EXAMPLE III

Example III is another non limiting example for a recording member suitable for imaging in accordance with the method of Fig. 2 where the IR radiation insolubilizes coating 14.

The following pre-coat was prepared:

resin - NeoCryl BT-20 (Zeneca- water-borne heat cured acrylic)	15
Isopropyl alcohol	1
cross linking reagent 880 Ammonia solution	1
Water	7
pH	8.5 - 9.0

The mixture was wire rod coated onto 100 micron clear polyester film to give a dried coating weight of 1 to 2 grams per square meter. the wet film was dried in an oven at 120°C for 10 minutes.

5 parts of the above solution were mixed with 10 parts of Stan-Tone 90WD01 Black (Harwick) and wire rod coated to a dry film weight of 3 grams per square meter. This was then dried at 120°C for 10 minutes.

Imaging was as described in Example I. The imaged member was then treated with a 10% solution of 2-butoxy ethanol in water. Alternatively, the member was treated with benzyl alcohol. In both cases, the solution removed the non exposed background areas, leaving black areas where the laser had imaged the image areas of the member. Dmax was 1.9 and the Dmin was 0.1.EXAMPLE IV

Example II is a non limiting example for a recording member suitable for imaging in accordance with the method of Fig. 4 where the IR radiation solubilized the image areas of coating 14.

The following pre-coat was prepared:

Adcote 102A (Morton polyester resin)	100
Catalyst F	5
Methyl Ethyl Ketone	30

This mixture was wire rod coated onto 100 micron clear polyester to a dry film of 2 grams per square meter and after an initial drying for 3 minutes in the oven at 120°C, it was left overnight before coating with the following composition:

Neorez 9679	50
Stantone Black	100
Neocryl CX-100 (Zeneca - polyfunctional aziridine crosslinker)	3.5
Ektasolve	2.5
Water	10
20% solution of Triton X100 (Rohm & Haas octoxynol-9 non-ionic wetting agent	1.6

The coating was dried for 10 minutes at 120°centigrade in an oven, resulting of a strong adherence of the pre-coat to the IR absorbing layer.

After imaging as in example I, the film was washed with benzyl alcohol. The background areas were unaffected by the washing process, but the areas where the laser had imaged were washed out. Dmax and Dmin were measured and found to be 3.3 and 0.4, respectively. The resulting recording film was a negative film.

EXAMPLE V

Example V is another non limiting example for a recording member suitable for imaging in accordance with the method of Fig. 2 where the IR radiation insolubilizes coating 14.

The following coating was prepared:

Desotech E045 (DSM - vinyl acrylate resin)	40.5
Mogul L carbon black (Cabot Carbons)	49.4
BK 7550 (Georgia Pacific - bisphenol A phenolic Resin)	10.0
Toluene	56.1

This mixture was milled in a ball-mill for 48 hours and then coated with a wire rod onto 100 micron polyester to a dry weight of 4 grams per square meter. After drying in an 120 degrees centigrade for 3 minutes, it was imaged as in Example I and developed by washing with gamma butyrolactone. The image areas were insoluble in the developer since they were affected by the heat produced during imaging to cross-link the combination of resins. However, the non imaged background areas washed out. Dmax was 2.6 and Dmin was 0.08.

EXAMPLE VI

Example VI is yet another non limiting example for a recording member suitable for imaging in accordance with the method of Fig. 2 where the IR radiation insolubilizes coating 14.

The following coating was prepared:

Alsynol RC12 (DSM - rosin-maleic resin esterified with entaerithritol)	5.2
Ebecryl 1259 (UCB Chemicals - aliphatic trifunctional urethane acrylate/methacrylate)	2.7
Irgacure 184 (Ciba-Geigy photoinitiator)	0.1
Benzoyl Peroxide	0.1
Mogul L carbon black	5.2
Ethyl Acetate	20
Ethyl alcohol	23

The mixture was ball milled for 48 hours to disperse the carbon black and then wire rod coated onto 100 micron polyester to a weight of 4 grams per square meter. It was imaged as in previous examples and washed with a 25% solution of ethanolamine. The background washed out and the image remained. Dmax was 2.8 and Dmin was 0.09.

It will be appreciated by persons skilled in the art that any of the recording members of the present invention provides in accordance with the methods for producing a recording film therefrom, a recording film suitable for preparing plates therefrom by the UV based contact process known in the art. It will be further be appreciated that the plates prepared employing the UV based contact process may be, for example, offset printing plates for offset printing presses, silk screen plates for the textile printing industry or plates for the Printed Circuit Board (PCB) industry.

It will also be appreciated by persons skilled in the art that the present invention is not limited by what has been particularly shown and described hereinabove. Rather the scope of the invention is defined by the claims which follow:

CLAIMS

1. An image recording member comprising:
   a. a substrate layer; and
   b. an infra red (IR) sensitive coating, the solubility of which being affected by impingement of IR radiation thereon.
2. A recording member according to claim 1 wherein said substrate layer is comprised substantially of polyester or polycarbonate with a thickness generally between 50 and 150 microns.
3. A recording member according to claim 1 or 2 wherein the transmissivity of said substrate to Ultra-Violet radiation is substantially higher than that of said coating.
4. A recording member according to any of the previous claims wherein the solubility of said coating increases upon impingement of said IR energy thereon, said pattern representing said image being a positive of said image.
5. A recording member according to claim 4 wherein said coating comprises:
   a. a resin; and
   b. an Infra-Red absorbing material.
6. A recording member according to claim 5 and also comprising a cross-linking agent.
7. A recording member according to claims 5 or 6 wherein said resin is selected from the group consisting of polyurethane

polyacrylate, polyester, vinylacrylate, phenolic resins and esterified resins

8. A recording member according to any of claims 5 - 7 wherein said Infra-Red absorbing material is selected from the group consisting of carbon black, nigrosine, phthalocyanine dye, metal diethylene and triaryl methane cationic salts.

9. A recording member according to any of claims 5 - 8 wherein said cross-linking agent is selected from the group consisting of benzoyl peroxide, aziridine cross-linker, ammonia and phenol formaldehyde cross-linking resin.

10. A recording member according to any of claims 1 - 3 wherein the solubility of said coating decreases upon impingement of said IR energy thereon, said pattern representing said image being a negative of said image.

11. A method for producing an image recording member comprising:

a. providing a substrate layer; and

b. coating said substrate layer with an infra red (IR) sensitive coating, the solubility of which being affected by impingement of IR radiation thereon.

12. A method according to claim 11, further comprising forming said substrate layer substantially from polyester or polycarbonate having a thickness generally between 50 and 150 microns.

13. A method according to claim 11 or 12, wherein said step of providing comprises providing a substrate layer with substantially higher transmissivity to UV radiation than said coating.

14. A method according to any of claims 11 - 13, wherein said step of coating comprises coating said substrate layer with a coating which solubility increases upon impingement of said IR energy thereon, said pattern representing said image being a positive of said image.

15. A method according to claim 14 wherein said step of coating comprises forming said coating from a resin and an Infra-Red absorbing material.

16. A method according to claim 15 wherein said step of forming further comprises the step of adding a cross-linking agent to said coating.

17. A method according to claim 15 or 16 wherein said forming comprises the step of selecting said resin from the group consisting of polyurethane, polyacrylate, polyester, vinylacrylate, phenolic resins and esterified resins.

18. A method according to any of claims 15 - 17 wherein said forming comprises the step of selecting said Infra-Red absorbing material from the group consisting of carbon black, nigrosine, phthalocyanine dye, metal diethylene and triaryl methane cationic salts.

19. A method according to any of claims 15 - 18 wherein said cross-linking agent is selected from the group consisting of benzoyl peroxide, aziridine cross-linker, ammonia and phenol formaldehyde cross-linking resin.

20. A recording member according to any of claims 11 - 13 wherein

coating whose solubility decreases upon impingement of said IR energy thereon, said pattern representing said image being a negative of said image.

21. A method for producing an image sensitive recording film comprising the step of:

    a. providing a recording member comprising an ultra violet transparent substrate layer and an infra red (IR) sensitive coating, the solubility of which being affected by impingement of IR radiation thereon;

    b. affecting the solubility of an area of said recording member; and

    c. washing said recording member so as to substantially remove said coating so as to expose said substrate layer, whereby a recording film with a representation of an image is formed.

22. A method according to claim 21 wherein said step of affecting the solubility of an areas of the coating of said recording member includes the step of increasing the solubility of said areas by impinging IR energy thereon.

23. A method according to claim 22 wherein said impinging is upon the background areas around the areas representing said image.

24. A method according to claim 22 wherein said impinging is upon said image areas.

25. A method according to claim 21 wherein said step of affecting the solubility of an areas of the coating of said recording member

includes the step of decreasing the solubility of the areas representing the image by impinging IR energy thereon.

26. A recording member produced in accordance with the method of any of claims 11 - 20.

27. A recording film produced in accordance with the method of any of claims 21 - 25.

28. A recording member according to any of claims 1 - 10 and 26, substantially as illustrated in any of the drawings.

29. A recording member according to any of claims 1 - 10 and 26, substantially as described hereinabove.

30. A method according to any of claims 10 - 25 substantially as illustrated in any of the drawings.

31. A method according to any of claims 10 - 25, substantially as described hereinabove.

32. A recording film according to claim 27, substantially as illustrated in any of the drawings.

33. A recording film according to claim 27, substantially as described hereinabove.

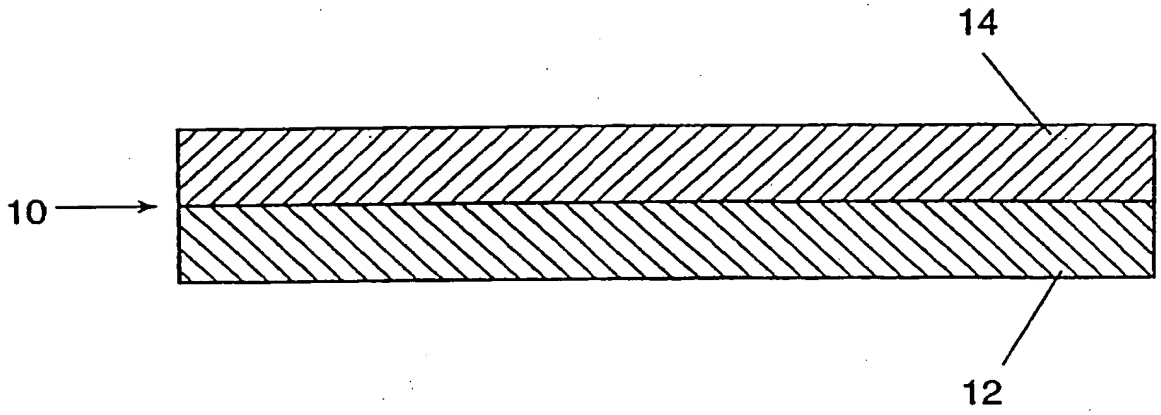

FIG. 1

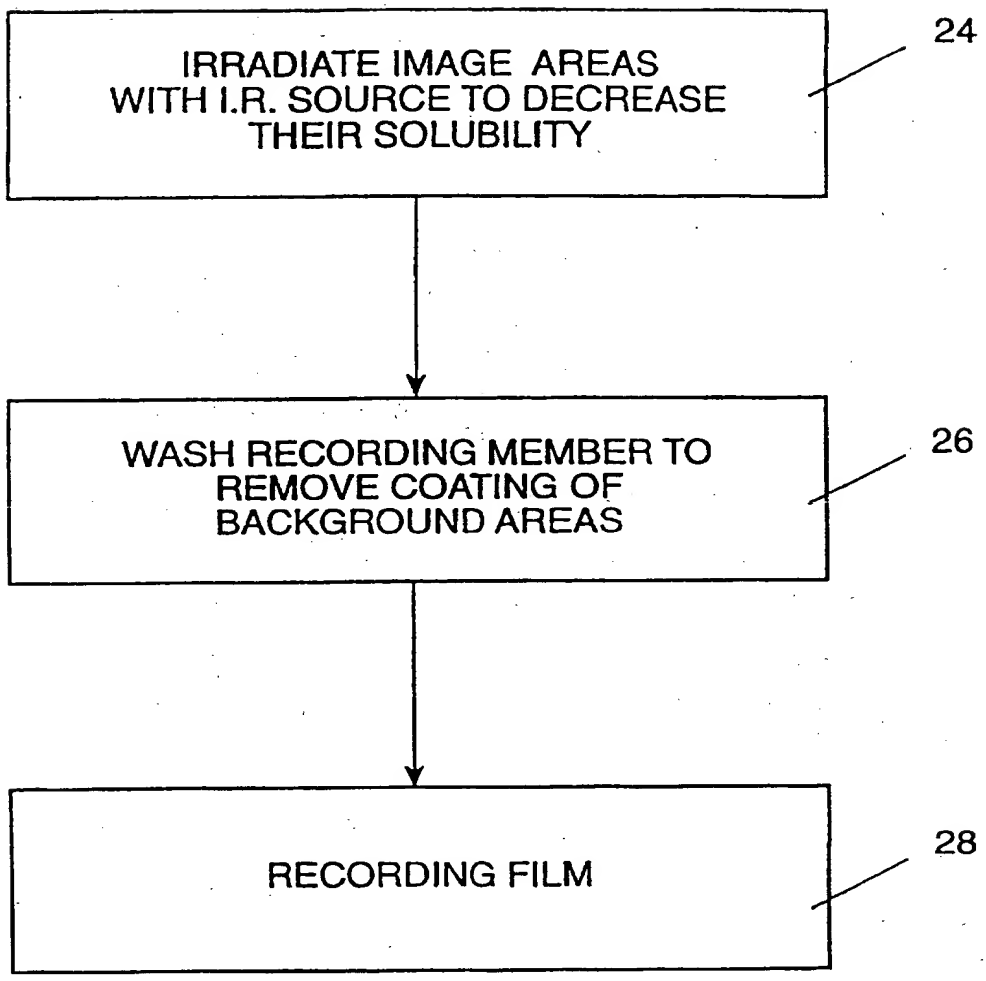

FIG. 2

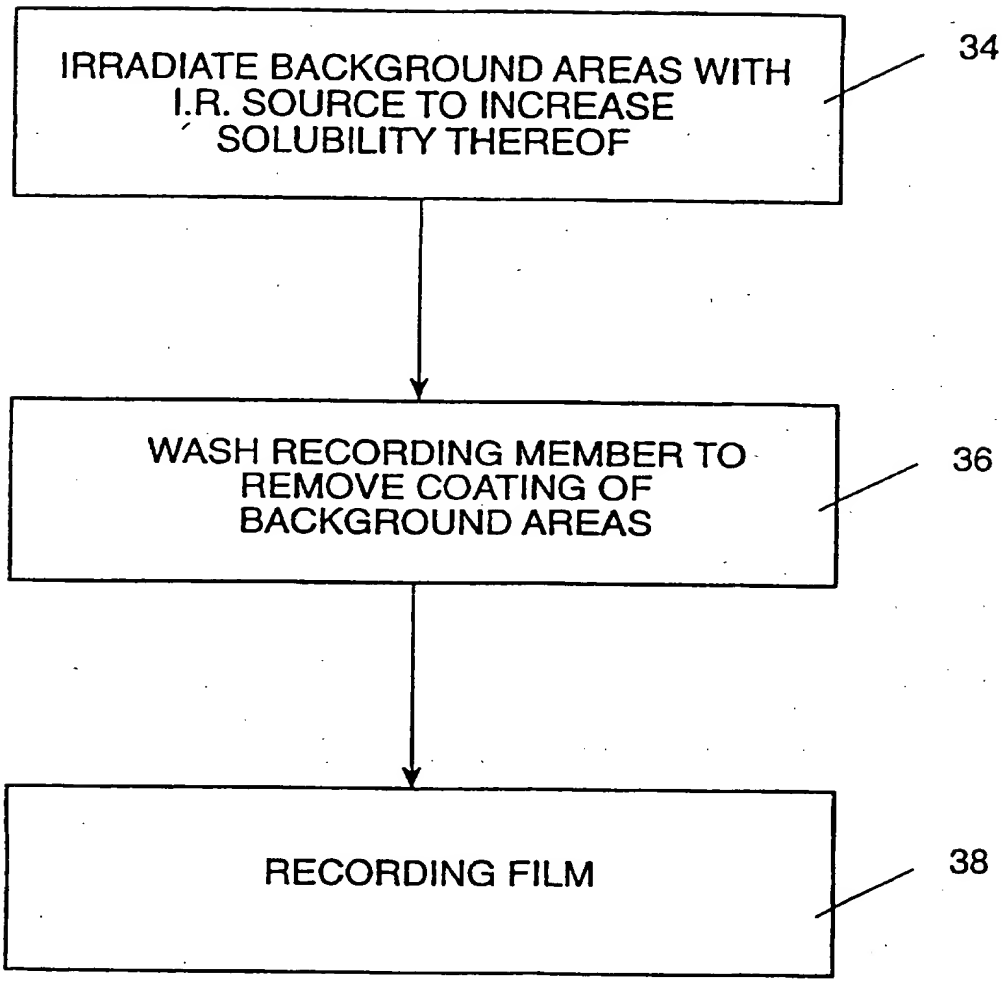

FIG. 3

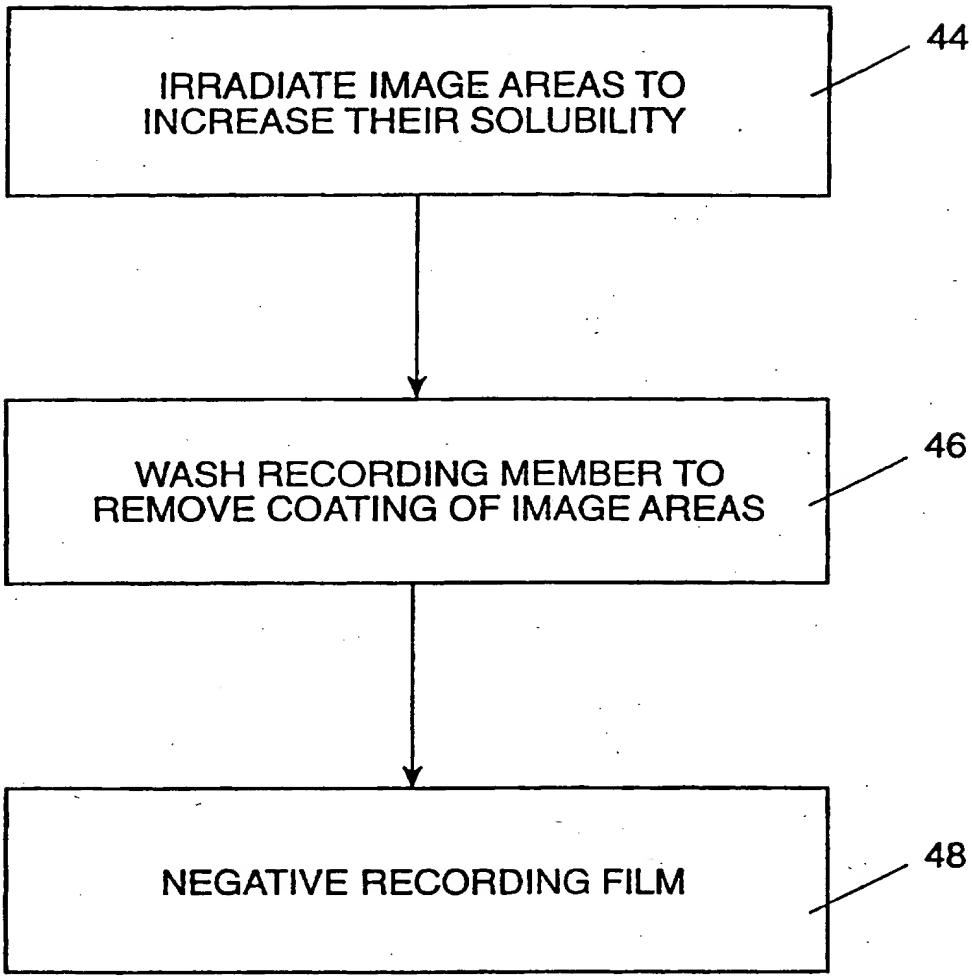

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL97/00164

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 27/36; B41M 5/20; B05D 1/36; G03C 5/00, 1/492; G02F 1/01
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) r to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/337, 412, 480; 503/201; 427/508, 407.1; 430/271.1, 325; 250/330

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: image recording member, infrared absorbing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,512,418 A (MA) 30 April 1996, entire document.	1-3, 11-13, 21-25
Y	US 5,262,275 A (FAN) 16 November 1993, col. 5-6, examples.	1-3, 11-13, 21-25
Y	US 4,920,036 A (TOTSUKA et al) 24 April 1990, col.3-4.	1-3, 11-13, 21-25
Y	US 3,580,719 A (BRINCKMAN) 25 May 1971, entire document.	1-3, 11-13, 21-25

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search	Date of mailing of the international search report
26 AUGUST 1997	12 SEP 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MARK A. CHAPMAN Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL97/00164

Box I Observations where certain claims were f und unsearchable (Continuation f item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 28-33
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The claims refer to multiple drawings and preceding claims that are not clearly defined and the scope and meaning of these claims cannot be ascertained.

3. ☒ Claims Nos.: 4-10, 14-20, and 26-33
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark n Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application Nc.
PCT/IL97/00164

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

428/337, 412, 480; 503/201; 427/508, 407.1; 430/271.1, 325; 250/330